



TITLE:

New Addition Reactions. (V) : Dimerization of Diketene

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ABSTRACTS

(2) In the decarboxylation of 3-aryl-2-oxazolidinones, the electronic effect of the substituent on the benzene ring indicates that the fission of the N-C bond of the urethane group in the 2-oxazolidinone ring is rate-determining. (3) The initial rate of the aliphatic amine-catalyzed decarboxylation of 3-aryl-2-oxazolidinones is of the pseudo-first-order; it also depends on the concentration and structure of the amine. A mechanism has been proposed which involves a nucleophilic attack of amine on the carbonyl-carbon atom. An amine having an hydroxyl or amino group on the β -carbon shows a large rate-acceleration; this suggests the simultaneous electrophilic participation by the active hydrogen of these groups. (4) The initial rate of the decarboxylation of 2-oxazolidinone itself, catalyzed by aliphatic amine, is of the second-order in oxazolidinone and of the first-order in amine. From this a concerted mechanism has been inferred, in which the amine acts as a nucleophile and the other oxazolidinone acts as an electrophile.

New Addition Reactions. (IV)

The Addition of Schiff Bases to Diketene

Ryohei ODA, Shunichi TAKASHIMA and Masaya OKANO

Bulletin of the Chemical Society of Japan, **35**, 1843 (1962)

Treatment of diketene with N-benzylidene-t-butylamine afforded a cyclic adduct, adduct, 1-t-butyl-6-phenyl-2,4-piperidinedione, in an excellent yield. Similar reactions with N-methylene-t-butylamine and N-methylenecyclohexylamine also gave the corresponding piperidinediones, but the yields were very low.

New Addition Reactions. (V)

Dimerization of Diketene

Ryohei ODA, Shunichi TAKASHIMA and Masaya OKANO

Bulletin of the Chemical Society of Japan, **36**, 476 (1963)

When diketene was treated with 5-10mol. % of aluminum tribromide in ethylene dichloride at 10-20°C for about thirty hours, a mixture of two dimers, 2,6-dimethyl- γ -pyrone-3-carboxylic acid and dehydroacetic acid (ratio 4:7), was obtained in ca. 60% yield without any formation of a polymeric by-product. This result is contrast to other Lewis acid-catalyzed reactions (cf. *Makromol. Chem.*, **39**, 243 (1960); **43**, 149 (1961)).
